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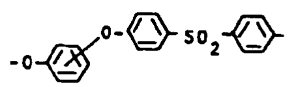
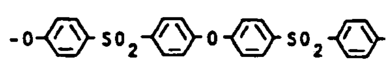
(54) Polyarylethersulphone copolymers.

(57) A polyarylethersulphone copolymers comprising 1 to 99 mole % of repeat units of formula

A 

and correspondingly 99 to 1 mole % of repeat units of formula

B 

The polyarylchlorosulphone copolymer of the invention may be controllably sulphonated to yield a hydrophilic sulphonated copolymer such that substantially all the units A are sulphonated after sulphonation and substantially all the units B remain non-sulphonated after sulphonation.

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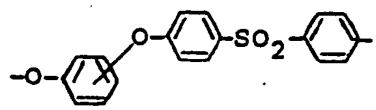
Croydon Printing Company Ltd.

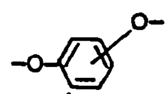
POLYARYLETHERSULPHONE COPOLYMERS

The present invention relates to certain polyarylethersulphone copolymers.

We have found that polyarylethersulphone polymers containing only the repeat units of formula

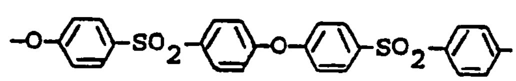


dissolve in concentrated sulphuric acid (98% w/w) and sulphonate very rapidly to give completely water-soluble products, probably due to the substitution of $-SO_2OH$ groups in all or most of the aromatic rings in the sub-units



of the polymer (see Examples 7 to 9), monosulphonation occurring in the case of the polymers with ortho or para disposed ether linkages in the sub-units and disulphonation occurring in the polymers with meta disposed linkages in the sub-units.

By contrast we have found that the polyarylethersulphones containing only the repeat unit of formula

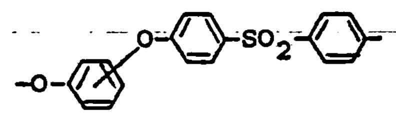
B 

are virtually non-susceptible to sulphonation in concentrated sulphuric acid (98% w/w), the sulphuric acid dissolving the polymer but not changing it, (see Example 10), even though other sulphonating agents such as oleum and chlorosulphonic acid, and even a mixture of concentrated sulphuric acid with a little oleum, completely sulphonate the polymer and/or degrade it (see Examples 11 and 12). Consequently polyaryl thersulphone

copolymers containing repeat units A and B may be controllably sulphonated in concentrated sulphuric acid (98% w/w) to give hydrophilic sulphonated copolymers (ranging up to completely water soluble polymers) by varying the proportion of the repeat unit B in the copolymer.

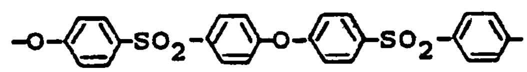
According to the present invention there is provided a polyarylethersulphone copolymer comprising 1 to 99 mole %, preferably 5 to 80 mole %, of repeat units of formula:

A

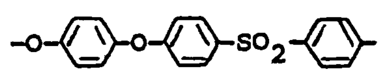


and correspondingly 99 to 1 mole %, preferably 95 to 20 mole %, of repeat units of formula:

B



The repeat units A preferably have para-disposed ether linkages, i.e. preferably have the formula



The polyarylethersulphone copolymers of the invention may be controllably sulphonated as indicated to yield a hydrophilic sulphonated copolymer such that substantially all the units A are sulphonated after sulphonation and substantially all the units B remain non-sulphonated after sulphonation.

The control of the sulphonation reaction should be such that the resulting copolymer preferably has a degree of hydrophilicity corresponding to a water absorption capacity at ambient temperature of about 2 weight % water absorption to complete solubility in water.

The sulphonated hydrophilic copolymers derived from the copolym rs of the invention (which preferably absorb

2-40 weight % water, particularly 5-30 weight % water, at ambient temperature) are potentially useful as membrane materials, e.g. for ultra-filtration processes, e.g. desalination and removal of micro-organisms, since they are not only hydrophilic in character but retain considerable strength even when containing a significant quantity of water (e.g. up to 20 weight % water) (see Example 5).

Ionomers of these sulphonate copolymers which are sulphonated with $-SO_2OH$ groups may be readily prepared e.g. by converting the $-SO_2OH$ groups to salts such as $SO_3^-M^+$ (where M = an alkali metal or NR_4, R being an alkyl group); these too have utility as hydrophilic polymers. Accordingly, the sulphonyl groups of the sulphonated copolymers derived from the copolymers of the invention preferably have the formula $-SO_2OY$ where Y is H, an alkali metal, or NR_4 where R is an alkyl group.

Copolymers having the repeat units A and B may be conveniently prepared by condensation of the appropriate dihydroxy phenol (e.g. hydroquinone, catechol or resorcinol), 4,4'-dihydroxydiphenylsulphone and 4,4'-dichlorodiphenylsulphone, and an alkali metal carbonate or bicarbonate in the presence of a sulphone or sulphoxide solvent, using the method of preparing polyarylene polyethers described in Canadian Patent 847 963.

The present invention is now illustrated by the following examples.

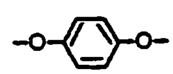
EXAMPLE 1

Copolymers of repeat units A (para disposed ether linkages in sub-units) and B of different compositions (varying from 25 mole % A to 66.7 mole % A and correspondingly 75 mole % B to 33.3 mole % B) were prepared by reacting appropriate proportions of hydroquinone and 4,4'-dihydroxydiphenylsulphone with 4,4'-dichlorodiphenylsulphone in the presence of K_2CO_3

and using diphenylsulphone as polymerisation solvent; the polymerisation temperatures were within the range 200-290°C. Substantially equimolar components of total bisphenol and dihalide were employed with a molar equivalent of K_2CO_3 being slightly in excess of twice that of the dihalide.

The copolymers were sulphonated as follows (using the copolymer of 25 mole % A/75 mole % B as a typical example). 20 g of copolymer was shaken for 18 hours with concentrated sulphuric acid (98% w/w) (110 ml) to give a very viscous solution. Further (50 ml) concentrated sulphuric acid was added and shaking continued for a further 18 hours (i.e. 36 hours in all). This solution was then poured into distilled water (800 ml) in a Waring blender, to give a white precipitate which was filtered and washed 3 times with fresh water in the blender, being separated by filtration after each wash. The product was dried overnight at about 65°C in a vacuum oven.

All the sulphonated copolymers after analysis by 220 MHz nmr spectroscopy indicated monosulphonation on substantially all of the sub-repeat units



in the polymer chain but no sulphonation on any of the repeat units B. All the sulphonated products were soluble in dimethyl formamide and dimethylsulphoxide.

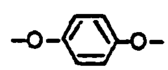
EXAMPLE 2

A copolymer of repeat units A (para disposed ether linkages in sub-units) and B containing 80 mole % A and 20 mole % B was prepared as described in Example 1. A sample (5 g) was shaken overnight with concentrated sulphuric acid (98% w/w) (20 ml). Further (20 ml) concentrated sulphuric acid was added and shaking continued for a further 24 hours. This solution was th n

poured into distilled water in a Waring blender to give a white precipitate which was filtered and washed 4 times with water, and dried overnight in a vacuum oven.

Copolymers of repeat units A (para disposed ether linkages in sub-units) and B containing respectively 5 mole % A/95 mole % B, 90 mole % A/10 mole % B, 40 mole % A/60 mole % B were sulphonated in a similar fashion to the copolymer 80 mole % A/20 mole % B, although starting from different quantities of copolymer and using different amounts of concentrated sulphuric acid.

The sulphonated products were analysed by 220 MHz spectroscopy which indicated monosulphonation on substantially all of the sub-repeat units



in the polymer chain but no sulphonation on any of the repeat units B.

EXAMPLE 3

The sodium salts of the sulphonated copolymers of Example 2 were prepared by neutralisation in excess NaOH solution. The neutralisation of the sulphonated 10 mole % A/90 mole % B copolymer is described as a typical example.

The sulphonated 10 mole % A/90 mole % B copolymer of Example 2 (50 g) was stirred overnight in a solution of NaOH (30 g) in water (600 ml). The mixture was then heated at 60-80°C all day and cooled to 40°C. The product was filtered, washed 4 times with water and oven dried.

The sodium contents of the sulphonated 10 mole % A/ 20 mole % B, 20 mole % A/80 mole % B and 40 mole % A/ 60 mole % B copolymers were determined using flame emission spectroscopy (FES) and confirmed the nmr spectroscopic analysis indicating that substantially all the units A had been monosulphonated. The results were as follows:

Molar Ratio A/B in copolymer	Na content f sulphonated copolymer found by FES	Monosulphonation of units A requires
10/90	0.53%	0.58%
20/80	1.20%	1.00%
40/60	2.30%	2.06%

EXAMPLE 4

The water absorption of the copolymers of Example 2 before sulphonation and after sulphonation, and also of the neutralised sulphonated copolymers of Example 3, were measured after steeping initially dry films of the copolymers (cast from solution in dimethyl formamide) in water for 24 hours at ambient temperature. The results were as follows:

Molar Ratio A/B in copolymer	Water absorption (weight %) of copolymer before sulphonation (Example 2)	Water absorption (weight %) of sulphonated copolymer (Example 2)	Water absorption of (weight %) of neutralised sulphonated copolymer (Example 3)
5/95	2.4	4.5	2.4
10/90	2.5	4.4	3.6
20/80	2.3	4.5	5.5
40/60	3.9	8.9	13.1
80/20	not measured	not measured	36.6

EXAMPLE 5

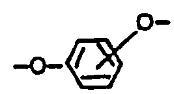
The sulphonated 40 mole % A/60 mole % B and 80 mole % A/20 mole % B copolymers of Example 2 were tested in the form of cast film for mechanical properties, both dry and after absorption of moisture. For comparison purposes a homopolymer containing units B only (not sulphonated) was also tested. The results were as follows:

Polymer Used		Water Content (wt %)	1% Secant Modulus (NMm^{-2})	Yield Stress (NMm^{-2})	Tensile Strength (NMm^{-2})	Elongation at break (%)
Homopolymer of units B	Dry	-	1450	-	74	8.2
	Wet	1.0	1350	-	-	-
Sulphonated copolymer 40 mole % A/60 mole % B	Dry	-	1700	68	62	10.1
	Wet	8.3	1500	45	-	-
Sulphonated copolymer 80 mole % A/20 mole % B	Dry	-	1750	59	47	14.7
	Wet	19.5	1030	32	26	32.1

(- indicates not measured)

EXAMPLE 6

A copolymer (5 g) of repeat units A (meta disposed ether linkages in sub-units) and B containing 40 mole % A and 60 mole % B was prepared following substantially the procedure described in Example 1 (using resorcinol in place of hydroquinone). 5 g of this copolymer was dissolved in concentrated sulphuric acid (98% w/w) and left for 36 hours. This solution was poured into distilled water to give a precipitate which was filtered, washed 3 times with water and oven dried. The product was analysed by 220 MHz spectroscopy and indicated disulphonation on substantially all of the sub-repeat units



in the polymer chain but no sulphonation on any of the repeat units B.

The water absorption of the sulphonated copolymer was measured after steeping an initially dry film of the copolymer (cast from solution in dimethyl formamide) in water for 24 hours at ambient temperature; the value obtained was 7.5 weight %.

EXAMPLE 7

A homopolymer of repeat unit A (para disposed ether linkages in sub-units) (10 g) was dissolved in concentrated sulphuric acid (98% w/w) with stirring and samples (50 ml) removed from time to time and precipitated in dilute sulphuric acid or saturated sodium sulphate; the polymer samples corresponding to the various times of sulphonation were analysed by 220 MHz nmr spectroscopy as solutions in dimethyl sulphoxide and found to have the following properties:

1 hour	85% of the units bore an $-SO_2OH$ group (isolated as Na salt).
2 hours	99% of the units bore an $-SO_2OH$ group (isolated as Na salt).
4.5 hours	100% of the units bore an $-SO_2OH$ group (isolated as Na salt).
23 hours	98% of the units bore an $-SO_2OH$ group (isolated as free acid).

Substantially all the sub-units bore one $-SO_2OH$ group.

EXAMPLE 8

A homopolymer of repeat unit A (ortho disposed ether linkages in sub-units) was sulphonated in concentrated sulphuric acid (98% w/w) and the product analysed by 220 MHz nmr spectroscopy as a solution in the concentrated sulphuric acid (the product would not precipitate by pouring the acid solution into water). As with the homopolymer of repeat unit A (para disposed ether linkages in sub-units) the product was found to have sulphonated rapidly with substantially all the sub-units bearing one $-SO_2OH$ group.

EXAMPLE 9

A homopolymer of repeat unit A (meta disposed ether linkages in sub-units) was sulphonated in concentrated sulphuric acid (98% w/w) and the product analysed by 220 MHz nmr spectroscopy as a solution in the concentrated sulphuric acid (the product would not precipitate by pouring the acid solution into water). As with the homopolymers of repeat unit A (para or ortho disposed ether linkages in the sub-units) the product was found to have sulphonated rapidly; substantially all the sub-units bore two $-SO_2OH$ groups however.

EXAMPLE 10

A homopolymer containing the repeat unit B (50 g) was dissolved in concentrated sulphuric acid (98% w/w) (200 ml), left for 72 hours, precipitated in dilute sulphuric acid, washed, macerated and dried. The infra-red and nmr spectra of the product showed it to be indentical with the starting material.

EXAMPLE 11

A homopolymer containing the repeat unit B (20 g) was added to chlorosulphonic acid (100 ml). Slight effeverence was apparent and white fumes were evolved. After standing overnight (the total time of the polymer in the acid being 20 hours), the solution was poured into 300 ml of concentrated sulphuric acid (98% w/w) and this solution then poured onto ice. A very fine precipitate resulted, which filtered very slowly and was washed once with water and then dried. The product appeared to be almost entirely soluble in water - indicating a high degree of sulphonation.

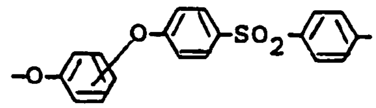
EXAMPLE 12

A homopolymer of repeat unit B (20 g) was mixed with oleum (150 ml) and left overnight. The resulting black solution still contained undissolved polymer and so the mixture was stirred for a further 5 hours, and then poured into water. No precipitate was obtained, but instead a brownish/orange solution was obtained. The product was discarded, being assumed to be highly sulphonated or entirely degraded.

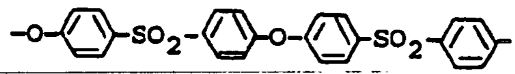
In another experiment, the homopolymer of repeat unit B (15 g) was dissolved in concentrated sulphuric acid (98% w/w); oleum (50 ml) was then added and the solution stirred for 30 minutes and then poured onto ice and left overnight. A rubbery white solid was precipitated and was washed and dried. This product was found to be highly sulphonated.

CLAIMS

1. A polyarylethersulphone copolymer comprising 1 to 99 mole % of repeat units of formula:

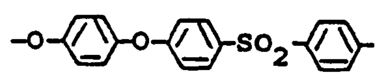
A 

and correspondingly 99 to 1% of repeat units of formula:

B 

2. A polyarylethersulphone copolymer according to claim 1 comprising 5 to 80 mole % of repeat units A and correspondingly 95 to 20 mole % of repeat units B.

3. A polyarylethersulphone copolymer according to either claim 1 or claim 2 wherein the units A have the formula



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